



April 12, 2016

Mr. Jim Harrington
Director, Remedial Bureau A
Division of Environmental Remediation
NYSDEC
625 Broadway
Albany, NY 12233-7012

**Re: NYSDEC Standby Engineering Contract D007625-27
WA # 27 Grumman Aircraft Engineering Corporation/Naval Weapons
Industrial Plant
NYSDEC Site #130003A/13000B Draft CSIA Results**

Dear Mr. Harrington;

Henningson, Durham & Richardson Architecture and Engineering, P.C. (HDR) offers the following notes on the draft Compound Specific Isotope Analysis (CSIA) Forensic Report for the Grumman Aerospace Bethpage Facility dated April 6, 2016 (attached), received from Pace Analytical (Pace). Much of the report provides information on methods and procedures used to perform the CSIA procedures. Site-specific results are presented starting on Page 12.

Summary

The report provides a summary of the analytical results of the volatile organic compound analyses and the forensic interpretation of the CSIA data resulting from the February 2016 sampling event. Trichloroethylene (TCE) and 1,4-dioxane were the contaminants of interest and a total of six monitoring wells were sampled during this event.

In summary, Pace has concluded that the TCE results are inconclusive, in that there are insufficient data to determine whether the TCE is emanating from one or more distinct sources. The 1,4-dioxane CSIA results indicate two distinct sources are present and that these commingle in downgradient wells.

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TCE results

TCE concentrations in the ground water taken from the wells sampled ranged from <1 (ND) to 590 ug/L. The CSIA results for TCE indicate that biodegradation may play a role in reducing VOC concentrations in ground water. There is also a possible indication that while the leading edge of the plume is being degraded, the center of it may be located in a less favorable environment for degradation to occur. The results for the limited number of samples collected do not suggest a nearby active source for the noted groundwater contamination. However, the report notes the results are inconclusive, due to a variety of confounding factors that may be influencing the isotopic signatures of the TCE detected. More study would be necessary to resolve these confounding factors, as discussed in the report.

1,4-dioxane Results

As we discussed would be possible during the planning phase for this sampling event, certain locations returned only low level or non-detect (ND) results, precluding CSIA being performed on one or more of the isotopes. This occurred with the 1,4-dioxane hydrogen isotope analyses, as noted in Table 3. Concentrations ranged from 3 to 116 ug/L in the groundwater samples collected with 4 of the 6 samples exhibiting concentrations less than 10 ug/L. For the two locations where hydrogen isotope results were obtained they did not show a significant difference and the data was qualified.

Despite the hydrogen isotope results, the 1,4-dioxane data are more definitive based on the carbon isotope analysis than those for TCE, indicating there may be two distinct sources of this contaminant. These also appear to commingle in the more downgradient wells that were sampled.

Conclusions

As noted in the report, this was intended to be the initial phase of sampling and analysis. The primary purpose of collecting this data was to evaluate the utility and value of forensics studies to identify the specific source(s) of the known groundwater contamination. The limited number of samples suggest this type of study holds value and as part of a well designed sampling program should be an element of additional work at this



site. As one example of additional work that could be done, source areas sampling and CSIA could provide the data needed to identify a particular source for the TCE and 1,4-dioxane detected in the wells, instead of just having evidence that there may be more than one site-specific source.

HDR can provide recommendations for additional sampling, should NYSDEC determine that is appropriate.

Please call with any questions. We appreciate the opportunity to work with you on this important project.

Sincerely,

Michael Lehtinen
Project Manager

Lisa K. Voyce
Professional Associate/Toxicologist

HDR



CSIA FORENSIC REPORT
GRUMMAN AEROSPACE BETHPAGE FACILITY
(NYSDEC Site Number 130003)
CSIA Projects #18232, 18233 & 18242

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April 6, 2016

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INTRODUCTION

Eight water samples (six groundwater samples and two trip blanks) were received at the Pace CSIA Center of Excellence on February 19th and 20th, 2016 for Compound Specific Isotope Analysis (CSIA) of dissolved volatile organic compounds (VOCs), specifically trichloroethene (TCE) and 1,4-dioxane (1,4-D). The samples were logged in as Pace CSIA Projects #18232, 18233 and 18242.

All samples were collected from the vicinity of Grumman Aerospace Bethpage Facility (GABF) located in the Town of Oyster Bay, Nassau County, New York. The GABF is currently listed on the New York State Registry of Inactive Waste Disposal Sites (NYSDEC Site #130003A/B/C) and includes the former Northrop Grumman Bethpage Facilities (NGBF), the former Naval Weapons Industrial Reserve Plant (NWIRP) and the Northrop Grumman-Steel Los Plant 2 (NGSLP).

The former GABF, including the NGBF and the NWIRP was situated on 605 acres in the Town of Oyster Bay. The Northrop Grumman Corporation was established in the early 1930s, and the NWIRP was established in 1941. Activities conducted at these facilities included engineering, administrative, research and development, and testing operations, as well as manufacturing operations for the Navy and the National Aeronautics and Space Administration (NASA). The manufacturing portion of the NGBF and the NWIRP are now closed. The facility is surrounded by industrial and commercial facilities, along with several residential communities.

Groundwater which has emanated from NGBF, NWIRP and the NGSLP contains hazardous chemicals (e.g., TCE & 1,4-D) above the maximum contaminants level. This groundwater is migrating to the south- southeast potentially impacting public water supply wells and other natural resources in its path.

As a Class 2 Registry Site, these sites pose a significant threat to the public health or environment and additional action is required to mitigate these risks.

The groundwater sampling plan (**Figure 1**) was provided by Henningson, Durham, and Richardson Architecture and Engineering P.C. (HDR). The goal of this initial study was to apply CSIA forensics to evaluate the status of contamination at the GABF site, and to see if there were connections between TCE and 1, 4-D detected in the groundwater samples collected from the vicinity of the GABF site and either NGBF, NWIRP or NGSLP.

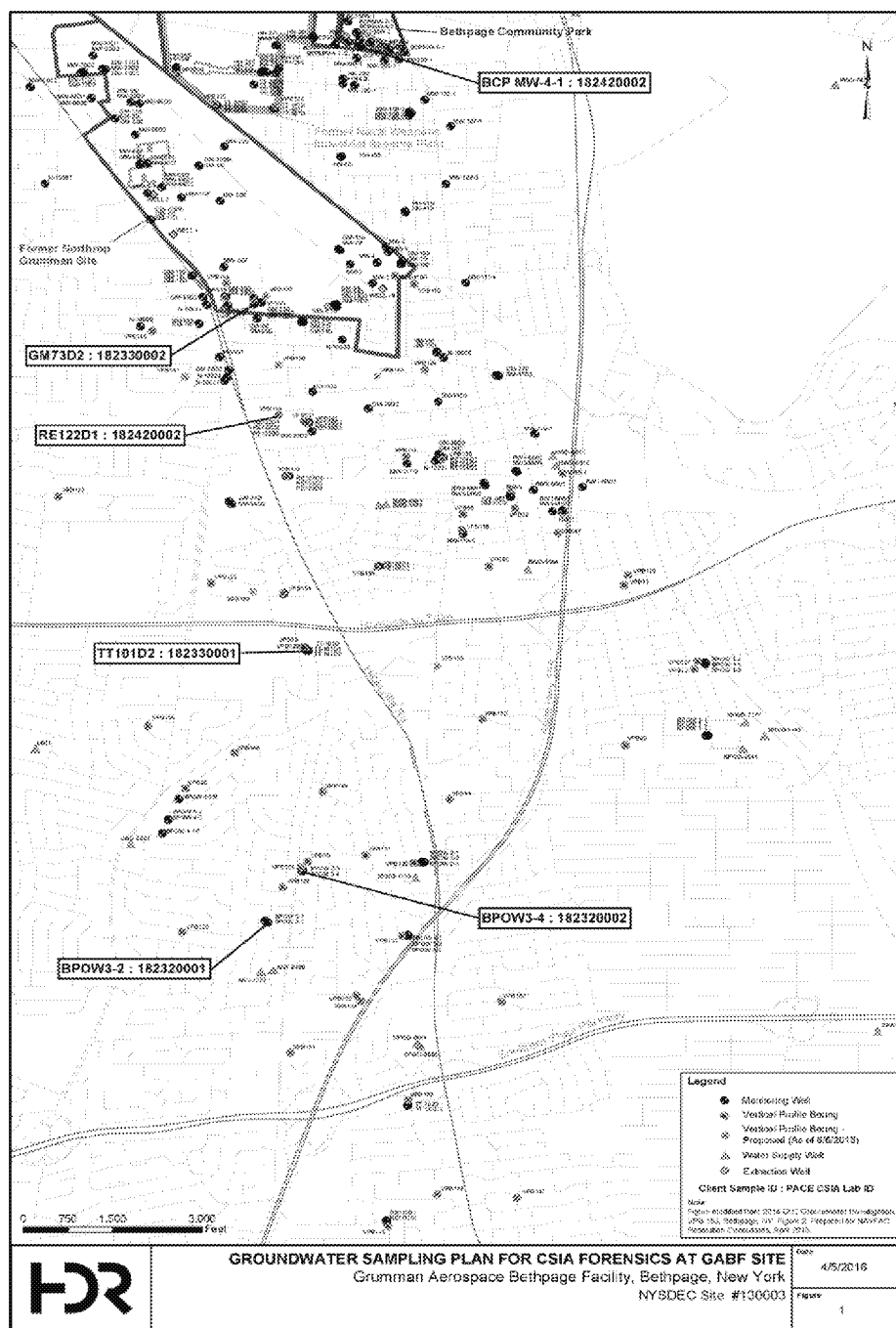


Figure 1 Groundwater sampling plan for CSIA forensics at the GABF Site

METHODOLOGY

Traditional analytical methods for CVOCs and molecular fingerprinting analysis, such as gas chromatograph-mass spectrometry (GC-MS), are unable to differentiate chlorinated solvents, such as TCE, or the solvent stabilizer 1,4-D, from different releases (sources), because: (1) unlike petroleum hydrocarbon products, which are mixtures of certain hydrocarbons with useful biomarkers, chlorinated solvents are often a single compound (e.g., TCE used as a cleaning solvent); and (2) chlorinated solvents from different sources appear chemically identical on traditional analytical instruments, such as a gas chromatograph-mass spectrometer (GC-MS).

However, chemically identical TCE or 1,4-D from different sources may have isotopic differences. CSIA of individual compounds in a sample mixture may help identify contaminants from the same source, or distinguish between contaminants from different sources.

The basis of the stable isotope analytical method is that elements exist in nature in more than one isotopic form (Clark and Fritz, 1997). For example, carbon exists in two stable isotopic forms: ^{12}C , with six protons and six neutrons, accounts for about 99% of carbon; ^{13}C , also with six protons but seven neutrons, accounts for about 1% of carbon. The ratio of the isotopes of an element is not the same in all naturally occurring compounds. There are small variations caused by the different atomic weights of the isotopes.

In a given compound, the isotopic composition is initially established when the compound is manufactured. It is a function of the isotopic composition of the raw materials; the chemical reactions employed in the manufacturing; any separation steps and all of the temperatures involved.

This results in a particular isotopic composition unique to the particular chemical lot. Over time a stable process that has a constant source of raw materials and uses a very rigid manufacturing procedure may produce many lots with minimal variance in the isotopic procedure. However, that isotopic composition may change significantly if there is even a small change in the manufacturing chain, such as a raw material supplier getting their materials from a different location. This makes CSIA an excellent tool for forensics, but it must be remembered that a single source of VOCs can have VOCs with more than one isotopic composition over time.

After manufacturing, the isotopic composition can be changed as the VOCs are used and as they are destroyed. It takes a little less energy to break a bond between a light isotope (^{12}C) and another atom than it takes to break a bond between a heavy isotope (^{13}C) and that same atom.

This leads to slightly slower reaction rates for heavy isotopes compared to light isotopes, and this in turn leads to a pooling, or increased percentage of heavy isotopes in the reactants of a reaction that breaks a bond and a pooling of light isotopes in the products of that reaction. This is called isotopic fractionation.

It should be kept in mind that while this effect is significant, reproducible and measureable it is very small and the absolute number of light isotopes reacting is still much larger than the number of heavy isotopes reacting. In fact, the isotopic fractionation effect is so small that it would require a very large figure to illustrate that effect at scale. Accordingly, a somewhat exaggerated example of isotopic fractionation is shown for a carbon-chlorine (C-Cl) bond in **Figure 2**.

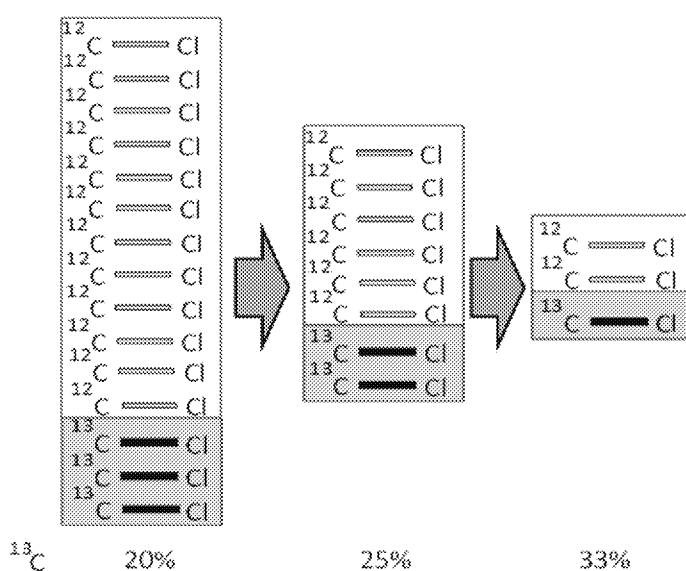


Figure 2 Example of isotopic fractionation

In CSIA, the ratio of $^{13}\text{C}/^{12}\text{C}$ (or “isotopic ratio”) is measured in each of the individual compounds in a mixture (e.g., TCE, cDCE and VC in a degrading TCE mixture). The isotopic composition is expressed as a $\delta^{13}\text{C}$ (‰) or “delta”, a convenient mathematical quantity linearly related to the isotopic ratio. The isotopic ratio of carbon is specified, not absolutely, but in relation to an internationally recognized standard (known as PeeDee Belemnite or “PDB”). A $^{13}\text{C}/^{12}\text{C}$ ratio that is more enriched in ^{13}C than the PDB standard has positive values, while ratios less enriched in ^{13}C have negative values.

For an isotopic ratio to significantly change, a bond must be broken. That means degradation of a compound is the only significant cause of increasing isotopic composition (deltas) for that compound. This makes CSIA an ideal tool to look for differences in the composition of minimally degraded chemicals that are otherwise indistinguishable.

For example, many investigations have documented that differences exist in the stable isotope ratios of solvents produced by various manufacturers (van Warmerdam, et al., 1995; Ertl, et al., 1998; Shouakar-Stash, et al., 2003). This is illustrated for PCE and TCE in Figure 3. Therefore stable isotope ratios determined by CSIA provide a method for potentially discriminating between contaminants from different releases (sources) and a method for identifying contaminants potentially from the same release (source) at complex sites. This knowledge can be used to help identify the parties that were responsible for the contamination (Morrison, 1999; Hunkeler, et al., 2004; Stark et al., 2003; Walker, et al., 2005). CSIA has been accepted as one line of evidence in litigation (U.S. EPA Guidance on CSIA, 2008).

Figure 3 shows different $\delta^{13}\text{C}$ and/or $\delta^{37}\text{Cl}$ values of PCE and TCE from four manufacturers (modified from multiple sources). In one case, the isotopic ratios for $^{13}\text{C}/^{12}\text{C}$ and $^{37}\text{Cl}/^{35}\text{Cl}$ were used to distinguish among three chlorinated solvent manufacturers (van Warmerdam, et al., 1995).

In a similar application, ^{13}C and ^{37}Cl were used to discriminate between two different pure phase chlorinated solvent batches obtained from various manufacturers using CSIA (Beneteau, et al., 1996).

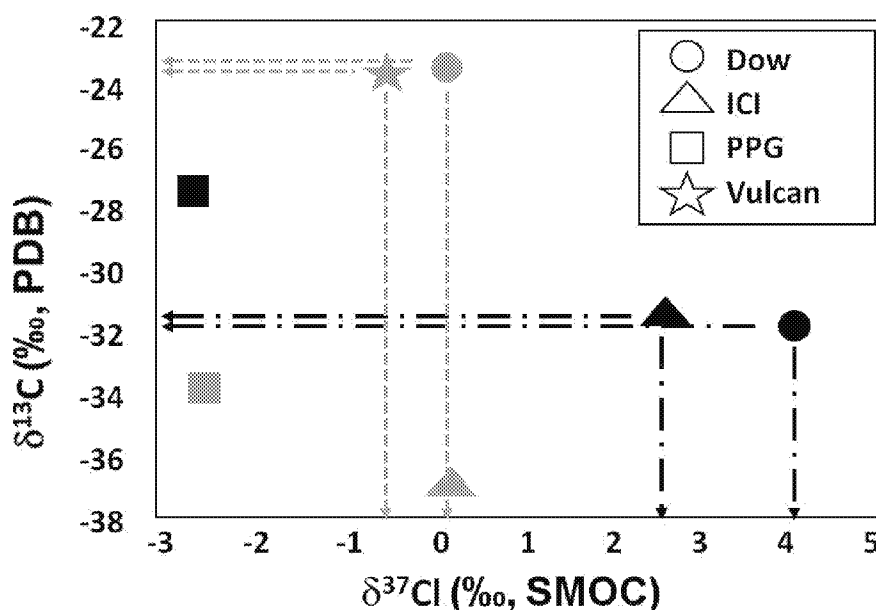


Figure 3 CSIA of PCE (grey) and TCE (black) of 4 manufacturers for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ ratios

Stable isotope analysis has been recognized by the U.S. Environmental Protection Agency (EPA) as an advanced site diagnostic tool which has an array of applications for organic pollutants, contaminated site investigation, and remediation.

The EPA Report, "A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis", Dec. 2008 describes the benefits and value of data provided by CSIA and contrasts the information provided by CSIA to information provided by long-term monitoring of concentrations of contaminants, or information provided from techniques where specific stable isotopes are added to environmental samples. After presenting the information summarized above, that report concludes that multiple isotope ratios determined by CSIA can potentially provide a method for discriminating between contaminants from different releases (sources) or a method for identifying solvents potentially from the same release (source) at complex sites.

Stable Isotope Ratios

Stable isotopes are measured as the ratio of the two most abundant isotopes of a given element. For carbon it is the ratio of ^{13}C , with a terrestrial abundance of 1.11%, to common ^{12}C which represents 98.89% of terrestrial carbon. Thus the $^{13}\text{C}/^{12}\text{C}$ ratio is about 0.011. Measuring an absolute isotope ratio requires rather sophisticated mass spectrometers. Rather than measuring a "true ratio", its "apparent ratio" can be easily measured by gas source mass spectrometry. To cancel the instrumental error due to operational variations in different laboratories and instruments, etc., a known reference can be measured on the same instrument at the same time (Clark and Fritz, 1997). The difference between the measured ratios of the sample and reference is expressed by the delta (δ) notation. δ values are expressed as parts per thousand or per mil (‰) difference from the reference for carbon:

$$\delta^{13}\text{C} = \left(\frac{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{Experiment}}}{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{standard}}} - 1 \right) \times 1000 \text{‰}$$

where the standard is the name of the reference used, in this case PDB, a belemnite rostrum from the Cretaceous Peedee formation of South Carolina. The standard, by definition, has a δ value of 0‰, and samples may have positive or negative δ values depending on whether the sample is enriched or depleted in the heavier isotope relative to the international standard. Positive δ values are referred to as being isotopic heavier and negative δ values are referred to as isotopic lighter. The sedimentary carbonate PDB lies at the heavy end of the naturally occurring carbon range, so most terrestrial materials on earth have negative δ values. For example, a δ value that has a positive value of +5‰, signifies that the sample has 0.5% more ^{13}C than the reference, or is enriched in ^{13}C by 5‰. Similarly, a sample that is depleted from the reference by this amount would be expressed as $\delta^{13}\text{C} = -5\text{‰ PDB}$.

It's important to remember the differences are relative to a standard, and for environmental purposes there is nothing particularly special about that standard. A $\delta^{13}\text{C} = +5\text{‰}$ is very different from a $\delta^{13}\text{C} = -5\text{‰}$, but the important point is that they differ by 10 ‰ and not that one is positive and one is negative.

The ratios for the other elements, such as hydrogen and chlorine, are expressed in the same way relative to their specific standards. For hydrogen isotopes, the accepted reference is Standard Mean Ocean Water (SMOW); and for chlorine isotope, it is Standard Mean Ocean Chloride (SMOC).

CSIA for Carbon and Hydrogen Isotopes

CSIA for carbon isotopes involves a multi-step process using GC-IRMS: (1) sample introduction to the gas chromatograph (GC), either by purge and trap procedure for volatile aqueous samples or direct injection for non-volatile target analytes previously extracted from the water, (2) separation of individual carbon-bearing compounds on a GC capillary column, (3) quantitative conversion of each compound to CO_2 in a high temperature combustion oven, (4) removal of H_2O produced in combustion, and (5) introduction of the CO_2 derived from each compound into the isotope ratio mass spectrometer (IRMS) for isotope analysis as shown in **Figure 4**.

After ionization of CO_2 , the mass spectrometer separates ions with different mass-to-charge ratios in space, allowing the simultaneous measurement of the ions with fixed Faraday cups. The high precision required in CSIA at the natural abundance level of stable isotopes can be achieved only with this simultaneous ion measurement. A typical GC-IRMS chromatogram by carbon CSIA is shown in **Figure 5**.

For hydrogen isotopes, the same process applies except for the conversion of each compound to H_2 and C in a higher temperature (oxygen free) oven, and introduction of the H_2 derived from each compound into the mass spectrometer for hydrogen isotope analysis.

CSIA for Chlorine Isotopes

Unlike carbon and hydrogen isotope CSIA, which have been available for decades, until recently, chlorine isotope analysis by traditional methods could not be carried out without lab-intensive, offline pretreatments to convert chlorinated compounds into methyl chloride (CH_3Cl). After such conversion, the chlorine isotope ratio is determined using a dual-inlet isotope ratio mass spectrometer. With care this technique can be used to achieve exceptional precision, often $\pm 0.1\text{‰}$. However this complex and laborious sample preparation process severely limits the sensitivity of this method.

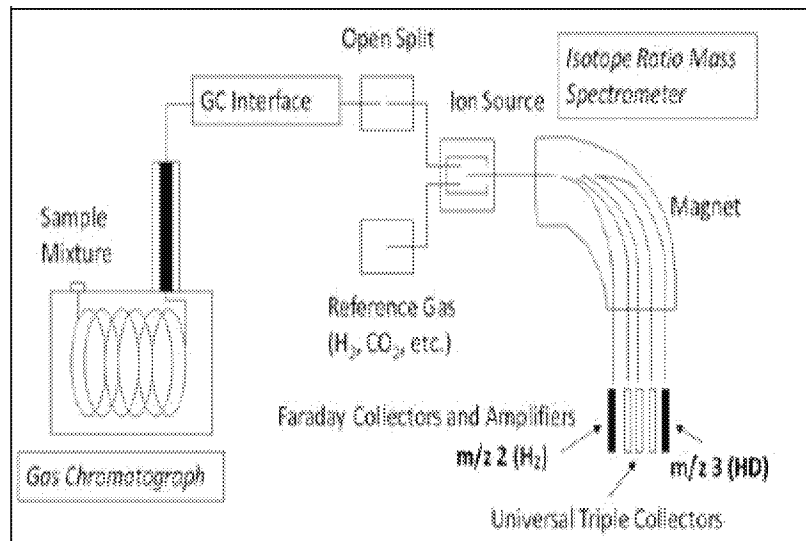


Figure 4 Schematic of the GC-IRMS and general procedure used in carbon and hydrogen CSIA

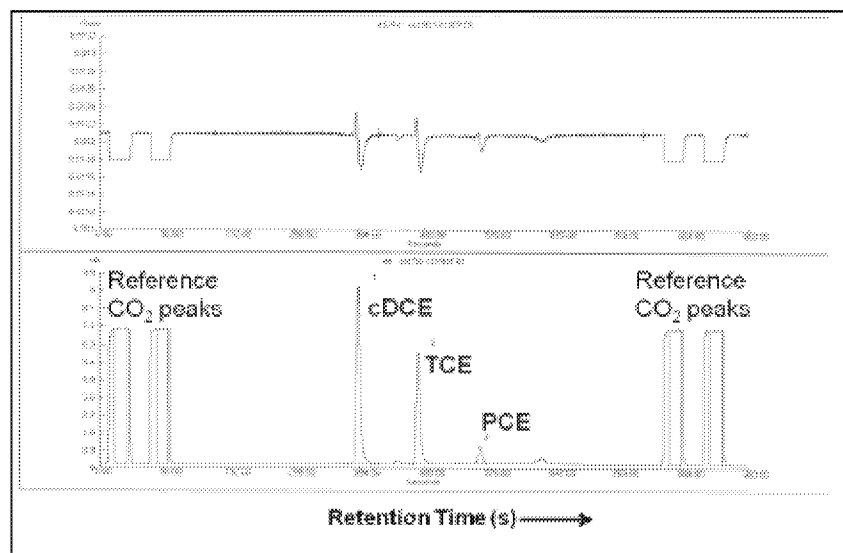


Figure 5 A typical GC-IRMS Chromatogram by Carbon-CSIA

Since 2009, chlorine isotopes of CVOCs, including PCE and TCE, have been analyzed using a modified method originally based on work of Sakaguchi-Söder, et al. (2007) and later optimized based on work of Jin, et al. (2011). This is a sensitive CSIA method for chlorine isotope of CVOCs by using gas chromatography coupled to a quadrupole mass spectrometer (GC-qMS). In contrast to carbon and hydrogen, the two stable isotopes of chlorine are two-mass units apart and both occur at relatively similar abundances (³⁵Cl at 75.78% and ³⁷Cl at 24.22%). These characteristics enable a scanning quadrupole MS to record mass spectral data precisely to calculate isotope ratios.

However, unlike an IRMS, which can detect several masses simultaneously, a GC-qMS has only one detector, which records masses selected consecutively. Therefore, instrument parameters of a quadrupole MS including dwell time, number of selected masses, etc., are crucial factors for the reproducibility and precision of chlorine CSIA using GC-qMS.

The measurement of chlorine isotopes by GC-qMS does not require off-line sample pretreatments, but requires complex mathematical data analysis to derive meaningful chlorine isotope ratios from mass spectra. The chlorine isotope ratios of target compound are calculated from the peak areas of selected molecular ions and fragment ions of the substances, using a set of mathematic equations.

Besides the evaluable schemes used to calculate chlorine isotope ratios, instrumental settings including split ratio, ionization energy, and dwell times are also evaluated to optimize the chlorine isotope measurement of chlorinated solvents.

Sample Preparation

All groundwater samples collected were preserved with HCl or sodium sulfite/sodium bisulfate as required during sample collection in the field. Seventeen VOA vials (40mL, HCl preserved) were collected for each sample, so both VOCs pre-screening and CSIA test for TCE could be performed. Two amber bottles (1L, sodium sulfite/sodium bisulfate preserved) were collected for each sample, so both 1,4-D concentration pre-screening and CSIA test for 1,4-D could be performed.

All samples received were checked for any discrepancy and noted on the chain of custody and QA/QC documents if present. All samples were kept in a dark refrigerator below 5°C while the CSIA analysts waited for the results of the VOC/1,4-D analysis to be completed.

When CSIA is performed for TCE on a sample, TCE is extracted from water samples using Purge & Trap (EPA Method 5030C). TCE is then desorbed from the trap and into a helium carrier gas flow. TCE and other VOCs, if present, are separated on the GC column, flushed in the carrier gas through the furnace, and carbon isotope ratios are measured in the IRMS. Multiple pulses of reference gas are injected during each sample run to calibrate CO₂ signals from the sample peaks (EPA Guidance on CSIA, Dec. 2008). For chlorine isotope analysis, separated TCE enter the ion source of mass spectrometer detector directly for analysis. Hydrogen isotope analysis of TCE is not performed, however, due to competition from HCl formation during the pyrolysis of TCE.

When CSIA is performed for 1,4-D on a sample, 1,4-D is extracted from water samples using Solid Phase Extraction tubes (Munch and Grimmett, EPA Method 522). Solvent (dichloromethane, DCM) eluted 1,4-D is concentrated before introduction into the GC injection port. After separation of the VOCs on the GC column the eluting gas flow is oxidized (for carbon measurements) or pyrolyzed (for hydrogen measurements) and the resulting gas stream of either CO₂ in helium or H₂ in helium is ready for isotope analysis in the IRMS (EPA Guidance on CSIA, Dec. 2008).

RESULTS AND DISCUSSION

Six groundwater samples with detectable TCE and/or 1,4-D were received for this initial CSIA study. Sampling locations and parameters for CSIA forensics are displayed in **Figure 1**. The concentrations of 1,4-D and VOCs were measured by Method EPA 522 & SW846 8260B, respectively and are shown in **Table 1**, below. Note that “Pace CSIA Lab ID” and “Client Sample ID” are rearranged in **Table 1** according to the natural groundwater flow path, which is towards the south-southeast.

Table 1 Concentrations of 1,4-D and select VOC contaminants in samples from the GABF site

Pace CSIA Lab ID	Client Sample ID	Concentrations of Contaminants (µg/L)							
		1,4-D	VC	cDCE	TCE	PCE	11DCA	111TCA	Freon-113
18242-2	BCP MW-4-1	116	390	390	99	1.5	18	4.5	<1
18233-2	GM73D2	7.6	<1	<1	33	1.4	<1	<1	<1
18242-1	RE122D1	12.9	<1	1.8	590	1.5	<1	<1	4.3
18233-1	TT101D2	4.1	<1	2.0	590	<1	<1	<1	19
18232-2	BPOW3-4	3	<1	<1	73	<1	<1	<1	<1
18232-1	BPOW3-2	6	<1	<1	<1	<1	<1	<1	<1

As seen in **Table 1**, contaminants were detected in the highest concentrations at locations between the presumed upgradient well, BCP MW-4-1 and the presumed downgradient well, TT101D2. TCE in well BCP MW-4-1 (99 µg/L) is being biodegraded into its daughter products cDCE (390µg/L) and then VC (390 µg/L). However, these daughter products of TCE were nearly absent in the two down gradient wells RE122D1 and TT101D2 (<1-2 µg/L). Other VOCs [e.g., 1,1,1-trichloroethane (111TCA) and 1,1-dichloroethane (11DCA)] were present in the well BCP MW-4-1, but were not detectable in the downgradient wells. Freon-113 was detected in the two downgradient wells RE122D1 and TT101D2 (at 4.3 and 19 µg/L, respectively) but not in the upgradient well.

1,4-D was often used as a stabilizer in 111TCA. 111TCA can be degraded through a variety of mechanisms, some biologic (Egli, et al., 1987; Galli, et al., 1989) and some abiotic (Gerken, et al., 1989).

While 1,4-D degradation has been observed at some sites, 1,4-D is much more recalcitrant than 111TCA (Mohr, et al., 2010). Thus, the 111TCA can degrade while the 1,4-D persists, and this could lead to the appearance of the 1,4-D in downgradient wells where there has been no measureable 111TCA. Alternately, 1,4-D is often found as an impurity in de-icing fluids, so its presence may not coincide with 111TCA. In addition, 1,4-D is completely water miscible and can migrate faster in groundwater than its associated parent plume (Mohr et al., 2010).

As shown in **Table 1**, except for the upgradient well BCP MW-4-1 (with 1,4-D detected at 116 µg/L), the 1,4-D detected in the other five monitoring wells at the GABF site was either close to or below 10 µg/L. 1,4-D was detected along with TCE in the downgradient well BPOW3-4, while in the further downgradient well BPOW3-2, only 1,4-D was detected.

CSIA Results from the GABF Site

Results of the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ of TCE and the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of 1,4-D are illustrated in **Table 2** and **Table 3**, respectively. Isotope ratios for certain samples could not be determined (labeled as ND) because the concentration of the target compound was too low to ensure reliable isotopic results. Standard precisions of CSIA for carbon and chlorine isotopes are both at $\pm 0.50\%$ (in PDB and SMOC, respectively). For compounds giving low signals, the errors increase. Precisions for such carbon and chlorine isotope analyses will be up to $\pm 2\%$ (in PDB and SMOC, respectively) and labeled with a J flag. Standard precision of CSIA for hydrogen isotopes is at $\pm 5\%$ (in SMOW). For compounds giving low signals, the errors increase. Precisions for such hydrogen isotope analyses will be up to $\pm 20\%$ (in SMOW) and labeled with a J flag.

Table 2 CSIA Results obtained for TCE in 6 samples from the GABF site

Pace	Client	Concentrations	$\delta^{13}\text{C}$	$\delta^{37}\text{Cl}$
Lab ID	Sample ID	(µg/L)	(‰ PDB)	(‰ SMOC)
18242-2	BCP MW-4-1	99	-21.13	-0.54
18233-2	GM73D2	33	-24.44	-2.75
18242-1	RE122D1	590	-23.90	-2.74
18233-1	TT101D2	590	-24.55	-2.63
18232-2	BPOW3-4	73	-22.62	-1.92
18232-1	BPOW3-2	<1	N/A	N/A

Degradation of TCE makes both $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ heavier in the remaining TCE, and the extent of the enrichment in the carbon is closely linked to the extent of the enrichment in the chlorine. Plots of $\delta^{37}\text{Cl}$ vs. $\delta^{13}\text{C}$ are based on the Rayleigh equation:

$$\delta = \delta_0 + \epsilon \ln \frac{C}{C_0} \quad \text{EQ 1}$$

Where δ_0 is the starting δ , ϵ is the enrichment factor, C is the concentration and C_0 is the starting concentration.

This equation applies for both $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$, though each has a different enrichment factor (ϵ_C and ϵ_{Cl} , respectively).

$$\delta^{13}\text{C} = \delta_0^{13}\text{C} + \epsilon_C \ln \frac{C}{C_0} \quad \text{EQ 2}$$

$$\delta^{37}\text{Cl} = \delta_0^{37}\text{Cl} + \epsilon_{Cl} \ln \frac{C}{C_0} \quad \text{EQ 3}$$

These equations can be combined to produce:

$$\delta^{37}\text{Cl} = \delta_0^{37}\text{Cl} - \frac{\epsilon_{Cl}}{\epsilon_C} \delta_0^{13}\text{C} + \frac{\epsilon_{Cl}}{\epsilon_C} \delta^{13}\text{C} \quad \text{EQ 4}$$

That equation gives $\delta^{37}\text{Cl}$ as a linear function of $\delta^{13}\text{C}$ with an intercept dependent only on the initial δ 's and ratio of the enrichment factors. To see if degradation could explain the variation seen in the TCE isotopic the data from Table 2 was plotted $\delta^{37}\text{Cl}$ vs $\delta^{13}\text{C}$ and the results are presented in Figure 6.

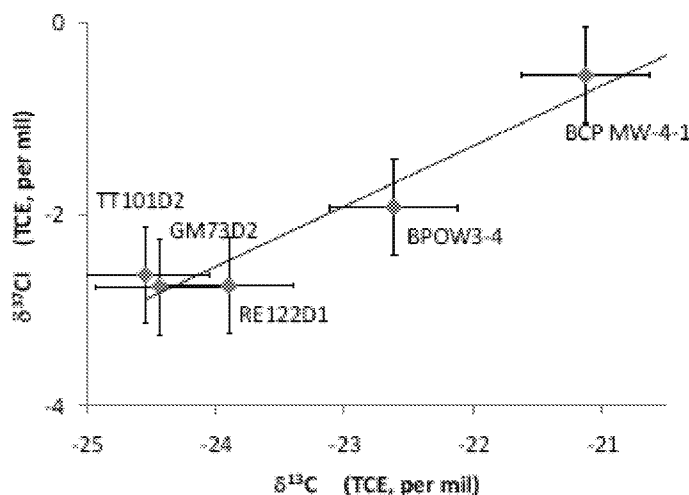


Figure 6 CSIA of TCE for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ ratios at five well locations

Figure 6 suggests that all of the variation can be explained by biodegradation. However, the extent of degradation does not seem to be related to the position downgradient. The most heavily degraded TCE is that furthest upgradient. This is typical of a mature source area where there is no longer a dissolved phase or an ongoing leak.

In this case organic carbon is often released with the TCE and that carbon fuels the source zone degradation. That organic carbon is rapidly consumed and does not travel far beyond the source area, so the degradation is very limited in the downgradient wells. The exception here is BPOW-3-4. That is the second most degraded of all of the wells but the farthest downgradient. If this is indeed all one plume, the water in that well has experienced conditions favorable to the degradation of TCE that the waters in the other sampled wells have not experienced.

This could be because that sample is taken from the leading edge of the plume, and as the plume advances newly encountered organic matter fuels degradation at the front of the plume. It is depleted after that, so the center of the plume is still largely undegraded.

To see if this is plausible it is appropriate to revisit EQ 4. The slope of the line predicted by EQ 4 is a ratio of the enrichment factors. Reductive dechlorination is the most common biodegradation mechanism for TCE, and Wiegert, et al (2013) have specified the ratio of enrichment factors for that process as 0.37 ± 0.11 . With a 90% one tailed confidence interval, the slope on the line in Figure 6 is 0.63 ± 0.16 . Thus within that limit they are statistical indistinguishable.

It can't be ruled out that there is more than one source and that the limited sample set and the extensive degradation in BCP-MW-4-1 and BPOW3-4 have made it such that this study can't identify the additional sources. Further, the possibility must be considered that these facilities shared a common TCE vendor. There is a possibility since these facilities operated at the similar time and were geographically very close. If they each had TCE from the same source, there would be no isotopic differences.

Table 3 CSIA Results obtained for 1,4-D in 6 samples from the GABF site

Pace	Client	Concentrations	$\delta^{13}\text{C}$	$\delta^2\text{H}$
Lab ID	Sample ID	($\mu\text{g/L}$)	(‰ PDB)	(‰ SMOW)
18242-2	BCP MW-4-1	116	-31.23	-59.69
18233-2	GM73D2	7.6	-35.87	ND
18242-1	RE122D1	12.9	-35.89	^J -57.93
18233-1	TT101D2	4.1	-32.65	ND
18232-2	BPOW3-4	3	-31.85	ND
18232-1	BPOW3-2	6	-31.81	ND

1,4-D CSIA Forensics: As shown in **Table 3**, carbon isotope ratios of 1,4-D divide all samples into 3 groups: 1,4-D detected in the up gradient well BCP MW-4-1 (highlighted in blue) has much heavier carbon isotope ratio compared with the samples highlighted in yellow, (-31‰ vs. -36‰; different of 4‰ to 5‰). Carbon CSIA ratios obtained for 1,4-D make up the third group composed of the three downgradient wells TT101D2, BPOW3-4, and BPOW3-2 (highlighted in orange) (which have $\delta^{13}\text{C}$ between the other two groups).

Most samples have concentrations of 1,4-D that are too low (<10 µg/L) for a reliable hydrogen CSIA. No significant difference is observed between 1,4-D obtained in samples BCP MW-4-1 and RE122D1 (-60‰ vs. -58‰), considering the analytical precision for hydrogen isotope analysis could be up to 20‰ for the low 1,4-D sample RE122D1 (12.9 µg/L). Therefore, following discussions focus on 1,4-D's carbon isotope fingerprinting.

Unlike TCE, 1,4-D is resistant to natural biodegradation in groundwater, and could retain its isotopic fingerprint in the groundwater system. Without considering any degradation induced isotope enrichment effect, multiple sources of 1,4-D release may exist at the GABF site as those highlighted in blue and yellow (**Table 3**), and those highlighted in orange may become co-mingled.

Up to 5‰ of enrichment in carbon isotope ratios is possible for 1,4-D, however, as degradation induced isotope enrichment factors for this emerging contaminant have not yet been well documented. Unless effective degradation of 1,4-D can be excluded at the site either with additional microbial study or with an analysis of historical 1,4-D concentrations, it would be too early to conclude that isotopic difference observed among the six samples from current study is simply due to multiple sources of 1,4-D release. More CSIA sampling locations should be tested for further 1,4-D isotope fingerprinting at the GABF site.

Summary

Based on the findings of this initial study, it appears that the TCE plume had a single source; however, that could not be absolutely determined because of a number of confounding issues (e.g., potential effect of biodegradation). It also appeared that there were two separate 1,4-D sources that co-mingled in the downgradient wells, but again that could not be unambiguously proven.

This study was intended to be a first step in the forensic process and it was always anticipated that a second phase would be necessary; the scope of which would be depending upon the initial study results. Overall, the most significant factor limiting the level of certainty in the conclusions made in this interpretation was the limited sample set size.

In the next phase, not only should the sample set provide a robust data set with which to test these preliminary conclusions, but also to test for variations throughout the extremely large area (i.e., roughly 5 square miles) and the range of depths (i.e., from 200 to greater than 800 feet below ground surface) that exhibit groundwater impacts from the GABF.

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April 5, 2016

Lisa Voyce
HDR
One International Plaza
10th Floor
Mahwah, NJ 07495

RE: **NYSDEC-GRUMMAN /147-275580-002**

Pace Workorder: 18232

Dear Lisa Voyce:

Enclosed are the analytical results for sample(s) received by the laboratory on Friday, February 19, 2016.

If you have any questions concerning this report, please feel free to contact me.

Sincerely,

Ruth Welsh 04/05/2016
Ruth.Welsh@pacelabs.com

Customer Service Representative

Enclosures

As a valued client we would appreciate your comments on our service.
Please email info@microseeps.com.

Total Number of Pages 7

Report ID: 18232 - 780512

CERTIFICATE OF ANALYSIS

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ED_002631A_00005127-00023



PAES Projects 18232, 18233 and 18242

April 4, 2016

Data for PAES projects 18232, 18233 and 18242 consisted of submitting data to HDR for four different analyses conducted on six samples. The analyses measured $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ on trichloroethene (TCE) and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ on 1,4-dioxane (14D). Each analysis will be discussed separately:

$\delta^{13}\text{C}$ of TCE – this analysis was performed in accord with the current SOP.

$\delta^{37}\text{Cl}$ of TCE – this analysis was performed in accord with the current SOP, but there was no study on record to justify using the analysis at concentrations below the Default Batch Standard Concentration (DBSC). However, the DBSC is 20 $\mu\text{g/l}$ while the lowest reportable TCE concentration in the subject samples is 33 $\mu\text{g/l}$. As such, it was not necessary to conduct the analysis at concentrations below the DBSC. This also made it unnecessary to have a study of the performance of this method below the DBSC.

$\delta^{13}\text{C}$ of 14D – this analysis was performed in two parts: The first step was an extraction of the 14D out of the water and into dichloromethane (DCM). The second part was measurement of that 14D/DCM solution on the isotopic mass spectrometer (IRMS).

Extraction: The procedure was conducted in accordance with the SOP. However, rather than having conducted a study of the minimum concentration of 14D in water that is appropriate for this test, effort was focused on testing that the extraction procedure produced no alteration of the $\delta^{13}\text{C}$. Internal studies had previously shown that concentrations of 14D in DCM of 40,000 $\mu\text{g/l}$ could be reliably measured when no extraction was done, and the extraction could be expected to provide concentration factors of 20,000. That was only useful if it did not alter $\delta^{13}\text{C}$. PAES focused their efforts on proving that there was no such alteration.

IRMS analysis of $\delta^{13}\text{C}$ of 14D in DCM: there were some readily observed deviations from the SOP but upon close inspection it was found that the criteria checked by the omitted steps could be tested by other pieces of data collected during the analyses. This led to the conclusion the data generated were absolutely valid, documentable and usable. For example, the SOP calls for a surrogate addition but it was deemed that a surrogate could crowd an already complex chromatogram and lead to poor integration of the 14D peak. A surrogate usually provides a check on the GC and IRMS functionality. The LCS_Lo and LCS_Hi were used as a check on the GC and the reference gas pulses in each sample were used as a check on the IRMS.

$\delta^2\text{H}$ of 14D – like the $\delta^{13}\text{C}$ analysis, this analysis was also performed in two parts: The first step was an extraction of the 14D out of the water and into dichloromethane (DCM). The second part was measurement of that 14D/DCM solution on the isotopic mass spectrometer (IRMS).

Extraction: The extracted aliquot was exactly as that prepared above for $\delta^{13}\text{C}$ of 14D. Again, a study had not been done to find what the minimum concentration was in water. Again, the concentration factor the extraction procedure could provide was quite large and it was clear

that the limit would be the inadvertent alteration of the $\delta^2\text{H}$ by the extraction procedure, so PAES focused their efforts on proving that there was no such alteration.

IRMS analysis of $\delta^2\text{H}$ of 14D in DCM: Just as in the measurement of $\delta^{13}\text{C}$ in the 14D, there were some readily observed deviations from the SOP but upon close inspection it was found that the criteria checked by the omitted steps could be tested by other pieces of data collected during the analyses. This led to the conclusion the data generated were absolutely valid, documentable and usable. The surrogate was omitted for the reason described above and the surrogates' purpose was served by the LCS_Lo, the LCS_Hi and the reference pulses in each analysis.

It should be noted that when it is said an "analysis was conducted in accordance with the SOP" that means there were no obvious, significant errors or deviations. An in-depth audit may find minor deviations but these would not affect the validity of the data. We feel that the service provided by these analyses was of very high caliber.

The following documentation will be provided to support these claims:

1. Raw data for $\delta^{13}\text{C}$ linearity analysis for TCE measurements
2. Calculations and analysis for $\delta^{13}\text{C}$ linearity for TCE
3. Raw data for $\delta^{13}\text{C}$ of TCE for field samples
4. Raw data for $\delta^{13}\text{C}$ of TCE for blanks, LCS's and sample duplicate
5. Raw data for $\delta^{37}\text{Cl}$ of TCE of field samples
6. Raw data for $\delta^{37}\text{Cl}$ of TCE of calibration samples
7. Calculations and analysis for $\delta^{37}\text{Cl}$ of TCE
8. Raw data for $\delta^{13}\text{C}$ linearity analysis for 14D measurements
9. Calculations and analysis for $\delta^{13}\text{C}$ linearity for 14D
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11. Raw data for $\delta^{13}\text{C}$ of TCE for blanks, LCS's and sample duplicate
12. Raw data for H_3 factor measurements
13. Raw data for $\delta^2\text{H}$ of 14D of field samples
14. Raw data for $\delta^2\text{H}$ of 14D for blanks, LCS's and sample duplicate
15. Raw data for TCE $\delta^{13}\text{C}$ PQL study
16. Calculations and Analysis for TCE $\delta^{13}\text{C}$ PQL study
17. Raw data for $\delta^{13}\text{C}$ test of 14D extraction procedure
18. Raw data for $\delta^2\text{H}$ test of 14D extraction procedure
19. Calculations and analysis of extraction procedure tests
20. SOPs

We are moving forward with all of the analyses and corrections necessary to provide documentation required in the SOPs in the next phase of this project as well as any future work.



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Phone: (412) 826-5245
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SAMPLE SUMMARY

Workorder: 18232 NYSDEC-GRUMMAN /147-275580-002

Lab ID	Sample ID	Matrix	Date Collected	Date Received
182320001	BPOW3-2-GW-021816	Water	2/18/2016 12:05	2/19/2016 11:00
182320002	BPOW3-4-GW-021816	Water	2/18/2016 13:00	2/19/2016 11:00

Report ID: 18232 - 780512

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Client: HDR
One International Blvd, 10th Floor
Mahwah, NJ 07495
Tel: 201.335.9330
Project: NYSDEC-Grumman
Project # 147-275580-002
Report to: Lisa Voyce
Email: Lisa.Voyce @ hdrinc.com

PACE Analytical CSIA Center
220 William Pitt Way
Pittsburgh, PA 15238
Tel: 412.826.5245
Report by: Dr. Yi Wang
Director, CSIA Center of Excellence
Cell: 609.721.2843
Email: yi.wang @ pacelabs.com

REPORT OF ENVIRONMENTAL FORENSICS ISOTOPE ANALYSES

Date Received: 2/19/2016

Date Reported: 3/18/2016

Samples for $\delta^{13}\text{C}$ (‰ PDB), $\delta^{37}\text{Cl}$ (‰ SMOC), and $\delta^2\text{H}$ (‰, SMOW) isotope ratios of TCE and 1,4-Dioxane

Pace CSIA Lab ID	Client's Sample ID Description	$\delta^{13}\text{C}$ TCE	$\delta^{37}\text{Cl}$ TCE	$\delta^2\text{H}$ TCE	$\delta^{13}\text{C}$ 1,4-D	$\delta^2\text{H}$ 1,4-D
18232-1	BPOW3-2-GW-021816	U -	U -	U -	-31.81 ^{JA}	-66.78
18232-2	BPOW3-4-GW-021816	-22.62	-1.92	U -	-31.85	^A -

Compound Specific Isotope Analysis (CSIA) for $\delta^{13}\text{C}/\delta^2\text{H}$ on Gas Chromatograph-Isotope Ratio Mass Spectrometer (GC-IRMS)
Chlorine Isotope Fast-Screening for $^{37}\text{Cl}/^{35}\text{Cl}$ on Gas Chromatograph-quadrupole Mass Spectrometer (GC-qMS)

^J - Target analyte produced a low peak signal and the result is considered usable to ± 2 ‰, but not the standard ± 0.5 ‰

^{JA} - Target analyte produced a low peak signal and the result is considered usable to ± 20 ‰, but not the standard ± 5 ‰

^U - Either not run or there was no peak corresponding to the target analyte

^A - The peak did not produce a reliable CSIA result due to sample matrix effect

TCE: Trichloroethene

1,4-D: 1,4-Dioxane

	$\delta^{13}\text{C}$	$\delta^{37}\text{Cl}$	$\delta^2\text{H}$	$\delta^{13}\text{C}$	$\delta^2\text{H}$
Quality Control STDs	TCE	TCE	TCE	1,4-D	1,4-D
QC-1	-26.46	-2.05	457	-33.25	-40.50
QC-2	-26.27	-2.62	464	-33.68	-40.17
Mean	-26.37	-2.34	461	-33.47	-40.34
Analytical Precision (1 σ)	0.13	0.40	5	0.30	0.23

Pace CSIA Forensic Isotope Services

Product or Dissolved Organics: Chlorinated Solvents, Oil, Extract, Fraction and Kerogen

3D-CSIA of ^{13}C , ^{37}Cl , and ^2H for PCE, TCE, DCE, MTBE, BTEX, 1,4-Dioxane, Alkanes, Gasoline and Oil; Bulk ^{13}C , ^2H , ^{18}O , ^{34}S , and ^{15}N

Gas Sample

Gas Composition and 2D-CSIA of ^{13}C and ^2H of C1 to C5; ^{13}C of CO_2 ; ^{14}C of C1 and CO_2 ; ^{34}S of H_2S ; ^{15}N and ^{18}O of N_2O gas

Water and Dissolved Inorganics

^2H , ^3H and ^{18}O ; ^{34}S and ^{18}O of dissolved sulfate; ^{34}S of dissolved H_2S

^{15}N and ^{18}O of dissolved Nitrate; ^{15}N of Ammonia; ^{13}C of dissolved CO_2 and Carbonate/Bicarbonate

Soil and Minerals

^{13}C , ^{18}O , ^{15}N , ^{34}S , D/H; ^{14}C of carbonate or organics

Post-Analysis Forensic Isotope Data Interpretation

Cooler Receipt Form

Client Name: HDR Project: NYSDEC - Grunman Lab Work Order: 18232

A. Shipping/Container Information (circle appropriate response)

Courier: FedEx UPS USPS Client Other: _____ Air bill Present: Yes No

Tracking Number: 804457522142

Custody Seal on Cooler/Box Present: Yes No Seals Intact: Yes No

Cooler/Box Packing Material: Bubble Wrap Absorbent Foam Other: _____

Type of Ice: Wet Blue None Ice Intact: Yes Melted

Cooler Temperature: 4°C Radiation Screened: Yes No Chain of Custody Present: Yes No

Comments: _____

B. Laboratory Assignment/Log-in (check appropriate response)

	YES	NO	N/A	Comment Reference non-conformance
Chain of Custody properly filled out	<input checked="" type="checkbox"/>			
Chain of Custody relinquished	<input checked="" type="checkbox"/>			
Sampler Name & Signature on COC	<input checked="" type="checkbox"/>			
Containers intact	<input checked="" type="checkbox"/>			
Were samples in separate bags	<input checked="" type="checkbox"/>			
Sample container labels match COC	<input checked="" type="checkbox"/>			
Sample name/date and time collected	<input checked="" type="checkbox"/>			
Sufficient volume provided	<input checked="" type="checkbox"/>			
PAES containers used	<input checked="" type="checkbox"/>			
Are containers properly preserved for the requested testing? (as labeled)	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
If an unknown preservation state, were containers checked? Exception: VOA's coliform			<input checked="" type="checkbox"/>	If yes, see pH form.
Was volume for dissolved testing field filtered, as noted on the COC? Was volume received in a preserved container?			<input checked="" type="checkbox"/>	

Comments: _____

Cooler contents examined/received by: LY Date: 2.19.15

Project Manager Review: AW Date: 2-20-16



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220 William Pitt Way
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Phone: (412) 826-5245
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April 5, 2016

Lisa Voyce
HDR
One International Plaza
10th Floor
Mahwah, NJ 07495

RE: **NYSDEC-GRUMMAN / 147-275580**

Pace Workorder: 18233

Dear Lisa Voyce:

Enclosed are the analytical results for sample(s) received by the laboratory on Friday, February 19, 2016.

If you have any questions concerning this report, please feel free to contact me.

Sincerely,

A handwritten signature in cursive script that reads 'Ruth Welsh'.

Ruth Welsh 04/05/2016
Ruth.Welsh@pacelabs.com

Customer Service Representative

Enclosures

As a valued client we would appreciate your comments on our service.
Please email info@microseeps.com.

Total Number of Pages 8

Report ID: 18233 - 780521

CERTIFICATE OF ANALYSIS

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PAES Projects 18232, 18233 and 18242

April 4, 2016

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$\delta^{13}\text{C}$ of TCE – this analysis was performed in accord with the current SOP.

$\delta^{37}\text{Cl}$ of TCE – this analysis was performed in accord with the current SOP, but there was no study on record to justify using the analysis at concentrations below the Default Batch Standard Concentration (DBSC). However, the DBSC is 20 $\mu\text{g/l}$ while the lowest reportable TCE concentration in the subject samples is 33 $\mu\text{g/l}$. As such, it was not necessary to conduct the analysis at concentrations below the DBSC. This also made it unnecessary to have a study of the performance of this method below the DBSC.

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$\delta^2\text{H}$ of 14D – like the $\delta^{13}\text{C}$ analysis, this analysis was also performed in two parts: The first step was an extraction of the 14D out of the water and into dichloromethane (DCM). The second part was measurement of that 14D/DCM solution on the isotopic mass spectrometer (IRMS).

Extraction: The extracted aliquot was exactly as that prepared above for $\delta^{13}\text{C}$ of 14D. Again, a study had not been done to find what the minimum concentration was in water. Again, the concentration factor the extraction procedure could provide was quite large and it was clear

that the limit would be the inadvertent alteration of the $\delta^2\text{H}$ by the extraction procedure, so PAES focused their efforts on proving that there was no such alteration.

IRMS analysis of $\delta^2\text{H}$ of 14D in DCM: Just as in the measurement of $\delta^{13}\text{C}$ in the 14D, there were some readily observed deviations from the SOP but upon close inspection it was found that the criteria checked by the omitted steps could be tested by other pieces of data collected during the analyses. This led to the conclusion the data generated were absolutely valid, documentable and usable. The surrogate was omitted for the reason described above and the surrogates' purpose was served by the LCS_Lo, the LCS_Hi and the reference pulses in each analysis.

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15. Raw data for TCE $\delta^{13}\text{C}$ PQL study
16. Calculations and Analysis for TCE $\delta^{13}\text{C}$ PQL study
17. Raw data for $\delta^{13}\text{C}$ test of 14D extraction procedure
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We are moving forward with all of the analyses and corrections necessary to provide documentation required in the SOPs in the next phase of this project as well as any future work.



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Phone: (412) 826-5245
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SAMPLE SUMMARY

Workorder: 18233 NYSDEC-GRUMMAN / 147-275580

Lab ID	Sample ID	Matrix	Date Collected	Date Received
182330001	TT101D2-GW-021816	Water	2/18/2016 16:05	2/19/2016 11:30
182330002	GM73D2-GW-021816	Water	2/18/2016 17:00	2/19/2016 11:30
182330003	TB-021816	Water	2/18/2016 07:00	2/19/2016 12:49

Report ID: 18233 - 780521

CERTIFICATE OF ANALYSIS

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ED_002631A_00005127-00033

Client: HDR
One International Blvd, 10th Floor
Mahwah, NJ 07495
Tel: 201.335.9330
Project: NYSDEC-Grumman
Project #: 147-275580
Report to: Lisa Voyce
Email: Lisa.Voyce @ hdrinc.com

PACE Analytical CSIA Center
220 William Pitt Way
Pittsburgh, PA 15238
Tel: 412.826.5245
Report by: Dr. Yi Wang
Director, CSIA Center of Excellence
Cell: 609.721.2843
Email: yi.wang @ pacelabs.com

REPORT OF ENVIRONMENTAL FORENSICS ISOTOPE ANALYSES

Date Received: 2/19/2016

Date Reported: 3/18/2016

Samples for $\delta^{13}\text{C}$ (‰ PDB), $\delta^{37}\text{Cl}$ (‰ SMOC), and $\delta^2\text{H}$ (‰, SMOW) isotope ratios of TCE and 1,4-Dioxane

Pace CSIA Lab ID	Client's Sample ID Description	$\delta^{13}\text{C}$ TCE	$\delta^{37}\text{Cl}$ TCE	$\delta^2\text{H}$ TCE	$\delta^{13}\text{C}$ 1,4-D	$\delta^2\text{H}$ 1,4-D
18233-1	TT101D2-GW-021816	-24.55	-2.63	^{JA} 228	-32.65	^A -
18233-2	GM73D2-GW-021816	-24.44	-2.75	^U -	-35.87	^{JA} -66.51
18233-3	TB-021816	^U -	^U -	^U -	^U -	^U -

Compound Specific Isotope Analysis (CSIA) for $\delta^{13}\text{C}/\delta^2\text{H}$ on Gas Chromatograph-Isotope Ratio Mass Spectrometer (GC-IRMS)

Chlorine Isotope Fast-Screening for $^{37}\text{Cl}/^{35}\text{Cl}$ on Gas Chromatograph-quadrupole Mass Spectrometer (GC-qMS)

^J - Target analyte produced a low peak signal and the result is considered usable to ± 2 ‰, but not the standard ± 0.5 ‰

^{JA} - Target analyte produced a low peak signal and the result is considered usable to ± 20 ‰, but not the standard ± 5 ‰

^U - Either not run or there was no peak corresponding to the target analyte

^A - The peak did not produce a reliable CSIA result due to sample matrix effect

TCE: Trichloroethene

1,4-D: 1,4-Dioxane

	$\delta^{13}\text{C}$	$\delta^{37}\text{Cl}$	$\delta^2\text{H}$	$\delta^{13}\text{C}$	$\delta^2\text{H}$
Quality Control STDs	TCE	TCE	TCE	1,4-D	1,4-D
QC-1	-26.46	-2.05	457	-33.25	-40.50
QC-2	-26.27	-2.62	464	-33.68	-40.17
Mean	-26.37	-2.34	461	-33.47	-40.34
Analytical Precision (1 σ)	0.13	0.40	5	0.30	0.23

Pace CSIA Forensic Isotope Services

Product or Dissolved Organics: Chlorinated Solvents, Oil, Extract, Fraction and Kerogen

3D-CSIA of ^{13}C , ^{37}Cl , and ^2H for PCE, TCE, DCE, MTBE, BTEX, 1,4-Dioxane, Alkanes, Gasoline and Oil; Bulk ^{13}C , ^2H , ^{18}O , ^{34}S , and ^{15}N

Gas Sample

Gas Composition and 2D-CSIA of ^{13}C and ^2H of C1 to C5; ^{13}C of CO_2 ; ^{14}C of C1 and CO_2 ; ^{34}S of H_2S ; ^{15}N and ^{18}O of N_2O gas

Water and Dissolved Inorganics

^2H , ^3H and ^{18}O ; ^{34}S and ^{18}O of dissolved sulfate; ^{34}S of dissolved H_2S

^{15}N and ^{18}O of dissolved Nitrate; ^{15}N of Ammonia; ^{13}C of dissolved CO_2 and Carbonate/Bicarbonate

Soil and Minerals

^{13}C , ^{18}O , ^{15}N , ^{34}S , D/H; ^{14}C of carbonate or organics

Post-Analysis Forensic Isotope Data Interpretation

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

220 William Pitt Way
Pittsburgh, PA 15238
412-826-5245

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Microseeps

18233

Page: 1 of 1
006171

Section A
Required Client Information:

Company: HDR
Address: 1 INTERNATIONAL BLVD
Methuen, MA 01465
Email To: LISA.VOYCE@HDR.COM
Phone: 201-335-9300
Requested Due Date/TAT: STANDARD

Section B
Required Project Information:

Report To: LISA VOYCE
Copy To: Mike Lentini
Purchase Order No.:
Project Name: WYSE DEC - COLUMBIA RD
Project Number: 147-275580

Section C
Invoice Information:

Attention: LISA VOYCE
Company Name: HDR
Address: 1 INTERNATIONAL BLVD
Pace Quote Reference:
Pace Project Manager: D. V. VOYCE, PhD
Pace Profile #:

REGULATORY AGENCY

NPDES

GROUND WATER

DRINKING WATER

UST

RCRA

OTHER

NYSDC

Site Location
STATE: NY

Section D Required Client Information										Requested Analysis Filtered (Y/N)										Pace Project No./ Lab I.D.																											
SAMPLE ID (A-Z, 0-9 / -) Sample IDs MUST BE UNIQUE Groundwater										Matrix Codes MATRIX / CODE Drinking Water Water Waste Water Product Soil/Solid Oil Wipe Air Tissue Other Groundwater										Matrix CODE (see valid codes to left)										SAMPLE TYPE (G=GRAB C=COMP)	COLLECTED		SAMPLE TEMP AT COLLECTION	# OF CONTAINERS	Preservatives										Analysis Test ↓	Y/N ↑	Residual Chlorine (Y/N)
										COMPOSITE START					COMPOSITE END/GRAB					DATE	TIME	DATE	TIME																								
1	TT161D2-GW-021814										G2G										G2G	2/18/16		19	Unpreserved H2SO4 HNO3 HCl TSP BAK Zinc Acetate & NaOH Other Seawater, Sulfide, Bismuth										2	Y											
2	GW352-GW-021814										G2G										G2G	2/18/16		19											7	Y											
3	TB-021814										TBG										TBG	2/18/16 0700		2											8	Y											
4																																															
5																																															
6																																															
7																																															
8																																															
9																																															
10																																															
11																																															
12																																															

Cooler Receipt Form

Client Name: HDR Project: NYSDEC Grumman Lab Work Order: 18233

A. Shipping/Container Information (circle appropriate response)

Courier: FedEx UPS USPS Client Other: _____ Air bill Present: Yes No

Tracking Number: 8044 5752 2120

Custody Seal on Cooler/Box Present: Yes No Seals Intact: Yes No

Cooler/Box Packing Material: Bubble Wrap Absorbent Foam Other: _____

Type of Ice: Yes Blue None Ice Intact: Yes Melted

Cooler Temperature: 2°C Radiation Screened: Yes No Chain of Custody Present: Yes No

Comments: _____

B. Laboratory Assignment/Log-in (check appropriate response)

	YES	NO	N/A	Comment Reference non-conformance
Chain of Custody properly filled out	<input checked="" type="checkbox"/>			
Chain of Custody relinquished	<input checked="" type="checkbox"/>			
Sampler Name & Signature on COC	<input checked="" type="checkbox"/>			
Containers intact	<input checked="" type="checkbox"/>			
Were samples in separate bags	<input checked="" type="checkbox"/>			
Sample container labels match COC Sample name/date and time collected	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		
Sufficient volume provided	<input checked="" type="checkbox"/>			
PAES containers used	<input checked="" type="checkbox"/>			
Are containers properly preserved for the requested testing? (as labeled)	<input checked="" type="checkbox"/>			
If an unknown preservation state, were containers checked? Exception: VOA's coliform			<input checked="" type="checkbox"/>	If yes, see pH form.
Was volume for dissolved testing field filtered, as noted on the COC? Was volume received in a preserved container?			<input checked="" type="checkbox"/>	

Comments: _____

Cooler contents examined/received by: LY Date: 2.19.16

Project Manager Review: BW Date: 2.20.16

NON-CONFORMANCE FORM

PAES Work Order #: 18233

Date: 2.19.16 Time of Receipt: 1130 Receiver: LY

Client: HDR

REASON FOR NON-CONFORMANCE

1. No time of collection on COC for 1st
2 samples. Time of 16:05 & 17:00
taken from bottles/vials
2. TB-021816 caps on vials were plastic
without septa.

ACTION TAKEN

Client name: _____

Date: _____ Time: _____

OK to proceed

Customer Service Initials: RW

Date: 2-20-16



Pace Analytical Energy Services LLC
220 William Pitt Way
Pittsburgh, PA 15238
Phone: (412) 826-5245
Fax: (412) 826-3433

April 5, 2016

Lisa Voyce
HDR
One International Plaza
10th Floor
Mahwah, NJ 07495

RE: **NYSDEC-GRUMMAN /147-275580-002**

Pace Workorder: 18242

Dear Lisa Voyce:

Enclosed are the analytical results for sample(s) received by the laboratory on Monday, February 22, 2016.

If you have any questions concerning this report, please feel free to contact me.

Sincerely,

A handwritten signature in cursive script that reads 'Ruth Welsh'.

Ruth Welsh 04/05/2016
Ruth.Welsh@pacelabs.com

Customer Service Representative

Enclosures

As a valued client we would appreciate your comments on our service.
Please email info@microseeps.com.

Total Number of Pages 1

Report ID: 18242 - 780531

CERTIFICATE OF ANALYSIS

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PAES Projects 18232, 18233 and 18242

April 4, 2016

Data for PAES projects 18232, 18233 and 18242 consisted of submitting data to HDR for four different analyses conducted on six samples. The analyses measured $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ on trichloroethene (TCE) and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ on 1,4-dioxane (14D). Each analysis will be discussed separately:

$\delta^{13}\text{C}$ of TCE – this analysis was performed in accord with the current SOP.

$\delta^{37}\text{Cl}$ of TCE – this analysis was performed in accord with the current SOP, but there was no study on record to justify using the analysis at concentrations below the Default Batch Standard Concentration (DBSC). However, the DBSC is 20 $\mu\text{g/l}$ while the lowest reportable TCE concentration in the subject samples is 33 $\mu\text{g/l}$. As such, it was not necessary to conduct the analysis at concentrations below the DBSC. This also made it unnecessary to have a study of the performance of this method below the DBSC.

$\delta^{13}\text{C}$ of 14D – this analysis was performed in two parts: The first step was an extraction of the 14D out of the water and into dichloromethane (DCM). The second part was measurement of that 14D/DCM solution on the isotopic mass spectrometer (IRMS).

Extraction: The procedure was conducted in accordance with the SOP. However, rather than having conducted a study of the minimum concentration of 14D in water that is appropriate for this test, effort was focused on testing that the extraction procedure produced no alteration of the $\delta^{13}\text{C}$. Internal studies had previously shown that concentrations of 14D in DCM of 40,000 $\mu\text{g/l}$ could be reliably measured when no extraction was done, and the extraction could be expected to provide concentration factors of 20,000. That was only useful if it did not alter $\delta^{13}\text{C}$. PAES focused their efforts on proving that there was no such alteration.

IRMS analysis of $\delta^{13}\text{C}$ of 14D in DCM: there were some readily observed deviations from the SOP but upon close inspection it was found that the criteria checked by the omitted steps could be tested by other pieces of data collected during the analyses. This led to the conclusion the data generated were absolutely valid, documentable and usable. For example, the SOP calls for a surrogate addition but it was deemed that a surrogate could crowd an already complex chromatogram and lead to poor integration of the 14D peak. A surrogate usually provides a check on the GC and IRMS functionality. The LCS_Lo and LCS_Hi were used as a check on the GC and the reference gas pulses in each sample were used as a check on the IRMS.

$\delta^2\text{H}$ of 14D – like the $\delta^{13}\text{C}$ analysis, this analysis was also performed in two parts: The first step was an extraction of the 14D out of the water and into dichloromethane (DCM). The second part was measurement of that 14D/DCM solution on the isotopic mass spectrometer (IRMS).

Extraction: The extracted aliquot was exactly as that prepared above for $\delta^{13}\text{C}$ of 14D. Again, a study had not been done to find what the minimum concentration was in water. Again, the concentration factor the extraction procedure could provide was quite large and it was clear

that the limit would be the inadvertent alteration of the $\delta^2\text{H}$ by the extraction procedure, so PAES focused their efforts on proving that there was no such alteration.

IRMS analysis of $\delta^2\text{H}$ of 14D in DCM: Just as in the measurement of $\delta^{13}\text{C}$ in the 14D, there were some readily observed deviations from the SOP but upon close inspection it was found that the criteria checked by the omitted steps could be tested by other pieces of data collected during the analyses. This led to the conclusion the data generated were absolutely valid, documentable and usable. The surrogate was omitted for the reason described above and the surrogates' purpose was served by the LCS_Lo, the LCS_Hi and the reference pulses in each analysis.

It should be noted that when it is said an "analysis was conducted in accordance with the SOP" that means there were no obvious, significant errors or deviations. An in-depth audit may find minor deviations but these would not affect the validity of the data. We feel that the service provided by these analyses was of very high caliber.

The following documentation will be provided to support these claims:

1. Raw data for $\delta^{13}\text{C}$ linearity analysis for TCE measurements
2. Calculations and analysis for $\delta^{13}\text{C}$ linearity for TCE
3. Raw data for $\delta^{13}\text{C}$ of TCE for field samples
4. Raw data for $\delta^{13}\text{C}$ of TCE for blanks, LCS's and sample duplicate
5. Raw data for $\delta^{37}\text{Cl}$ of TCE of field samples
6. Raw data for $\delta^{37}\text{Cl}$ of TCE of calibration samples
7. Calculations and analysis for $\delta^{37}\text{Cl}$ of TCE
8. Raw data for $\delta^{13}\text{C}$ linearity analysis for 14D measurements
9. Calculations and analysis for $\delta^{13}\text{C}$ linearity for 14D
10. Raw data for $\delta^{13}\text{C}$ of 14D for field samples
11. Raw data for $\delta^{13}\text{C}$ of TCE for blanks, LCS's and sample duplicate
12. Raw data for H_3 factor measurements
13. Raw data for $\delta^2\text{H}$ of 14D of field samples
14. Raw data for $\delta^2\text{H}$ of 14D for blanks, LCS's and sample duplicate
15. Raw data for TCE $\delta^{13}\text{C}$ PQL study
16. Calculations and Analysis for TCE $\delta^{13}\text{C}$ PQL study
17. Raw data for $\delta^{13}\text{C}$ test of 14D extraction procedure
18. Raw data for $\delta^2\text{H}$ test of 14D extraction procedure
19. Calculations and analysis of extraction procedure tests
20. SOPs

We are moving forward with all of the analyses and corrections necessary to provide documentation required in the SOPs in the next phase of this project as well as any future work.



Pace Analytical Energy Services LLC
220 William Pitt Way
Pittsburgh, PA 15238
Phone: (412) 826-5245
Fax: (412) 826-3433

SAMPLE SUMMARY

Workorder: 18242 NYSDEC-GRUMMAN /147-275580-002

Lab ID	Sample ID	Matrix	Date Collected	Date Received
182420001	RE122D1-GW-021916	Water	2/19/2016 10:40	2/22/2016 08:30
182420002	BCP MW-4-1	Water	2/19/2016 13:00	2/22/2016 08:30
182420003	TB-021916	Water	2/19/2016 07:00	2/22/2016 08:30

Report ID: 18242 - 780531

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Client: HDR
One International Blvd, 10th Floor
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Project: NYSDEC-Grumman
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Report to: Lisa Voyce
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Report by: Dr. Yi Wang
Director, CSIA Center of Excellence
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Email: yi.wang @ pacelabs.com

REPORT OF ENVIRONMENTAL FORENSICS ISOTOPE ANALYSES

Date Received: 2/20/2016

Date Reported: 3/18/2016

Samples for $\delta^{13}\text{C}$ (‰ PDB), $\delta^{37}\text{Cl}$ (‰ SMOC), and $\delta^2\text{H}$ (‰, SMOW) isotope ratios of TCE and 1,4-Dioxane

Pace CSIA Lab ID	Client's Sample ID Description	$\delta^{13}\text{C}$ TCE	$\delta^{37}\text{Cl}$ TCE	$\delta^2\text{H}$ TCE	$\delta^{13}\text{C}$ 1,4-D	$\delta^2\text{H}$ 1,4-D
18242-1	RE122D1-GW-021916	-23.90	-2.74	^{JA} 246	-35.89	^J -57.93
18242-2	BCP MW-4-1	-21.13	-0.54	^{JA} -58	-31.23	-59.69
18242-3	TB-021916	U	U	U	U	U

Compound Specific Isotope Analysis (CSIA) for $\delta^{13}\text{C}/\delta^2\text{H}$ on Gas Chromatograph-Isotope Ratio Mass Spectrometer (GC-IRMS)
Chlorine Isotope Fast-Screening for $^{37}\text{Cl}/^{35}\text{Cl}$ on Gas Chromatograph-quadrupole Mass Spectrometer (GC-qMS)

^J - Target analyte produced a low peak signal and the result is considered usable to ± 2 ‰, but not the standard ± 0.5 ‰

^{JA} - Target analyte produced a low peak signal and the result is considered usable to ± 20 ‰, but not the standard ± 5 ‰

^U - Either not run or there was no peak corresponding to the target analyte

^A - The peak did not produce a reliable CSIA result due to sample matrix effect

TCE: Trichloroethene

1,4-D: 1,4-Dioxane

	$\delta^{13}\text{C}$	$\delta^{37}\text{Cl}$	$\delta^2\text{H}$	$\delta^{13}\text{C}$	$\delta^2\text{H}$
Quality Control STDs	TCE	TCE	TCE	1,4-D	1,4-D
QC-1	-26.46	-2.05	457	-33.25	-40.50
QC-2	-26.27	-2.62	464	-33.68	-40.17
Mean	-26.37	-2.34	461	-33.47	-40.34
Analytical Precision (1 σ)	0.13	0.40	5	0.30	0.23

Pace CSIA Forensic Isotope Services

Product or Dissolved Organics: Chlorinated Solvents, Oil, Extract, Fraction and Kerogen

3D-CSIA of ^{13}C , ^{37}Cl , and ^2H for PCE, TCE, DCE, MTBE, BTEX, 1,4-Dioxane, Alkanes, Gasoline and Oil; Bulk ^{13}C , ^2H , ^{18}O , ^{34}S , and ^{15}N

Gas Sample

Gas Composition and 2D-CSIA of ^{13}C and ^2H of C1 to C5; ^{13}C of CO_2 ; ^{14}C of C1 and CO_2 ; ^{34}S of H_2S ; ^{15}N and ^{18}O of N_2O gas

Water and Dissolved Inorganics

^2H , ^3H and ^{18}O ; ^{34}S and ^{18}O of dissolved sulfate; ^{34}S of dissolved H_2S

^{15}N and ^{18}O of dissolved Nitrate; ^{15}N of Ammonia; ^{13}C of dissolved CO_2 and Carbonate/Bicarbonate

Soil and Minerals

^{13}C , ^{18}O , ^{15}N , ^{34}S , D/H; ^{14}C of carbonate or organics

Post-Analysis Forensic Isotope Data Interpretation

Cooler Receipt Form

Client Name: HDR Project: NYSDEC - Lab Work Order: 18242
Gramman

A. Shipping/Container Information (circle appropriate response)

Courier: FedEx UPS USPS Client Other: _____ Air bill Present: Yes No

Tracking Number: 8044 5752 2110

Custody Seal on Cooler/Box Present: Yes No Seals Intact: Yes No

Cooler/Box Packing Material: Bubble Wrap Absorbent Foam Other: _____

Type of Ice: Yes Blue None Ice Intact: Yes Melted

Cooler Temperature: 50C Radiation Screened: Yes No Chain of Custody Present: Yes No

Comments: _____

B. Laboratory Assignment/Log-in (check appropriate response)

	YES	NO	N/A	Comment Reference non-conformance
Chain of Custody properly filled out	<input checked="" type="checkbox"/>			
Chain of Custody relinquished	<input checked="" type="checkbox"/>			
Sampler Name & Signature on COC	<input checked="" type="checkbox"/>			
Containers intact	<input checked="" type="checkbox"/>			
Were samples in separate bags	<input checked="" type="checkbox"/>			
Sample container labels match COC	<input checked="" type="checkbox"/>			
Sample name/date and time collected	<input checked="" type="checkbox"/>			
Sufficient volume provided	<input checked="" type="checkbox"/>			
PAES containers used	<input checked="" type="checkbox"/>			
Are containers properly preserved for the requested testing? (as labeled)	<input checked="" type="checkbox"/>			
If an unknown preservation state, were containers checked? Exception: VOA's coliform			<input checked="" type="checkbox"/>	If yes, see pH form.
Was volume for dissolved testing field filtered, as noted on the COC? Was volume received in a preserved container?			<input checked="" type="checkbox"/>	

Comments: _____

Cooler contents examined/received by: LY Date: 2.22.16

Project Manager Review: EW Date: 2.22.16